Interactions in saccharide/cation/water systems: Insights from density functional theory

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A B S T R A C T

Interactions between saccharides and ions in aqueous solutions are of great importance in many fields (chemistry, physico-chemistry, biology, food industries). Thus, this work proposes to develop a methodology dealing with the characterization and the understanding of interactions between saccharides and cations in presence of water molecules, by a quantum mechanics approach. In the first part, the saccharide hydration properties (xylose, glucose, sucrose) in pure water are determined. Results show that the saccharide coordination numbers, as well as the saccharides hydration enthalpy, increase with the saccharide hydrophilic group number. In the second part, the influence of cations on saccharides hydration properties, and inversely, is evaluated. In saccharide/cation/water systems, the decrease in hydration enthalpy of cations and saccharides shows that both species are dehydrated and that saccharide dehydration depends on the nature of the cation. The dehydration sequence of saccharides was explained from the study of saccharide/cation interactions.

1. Introduction

More than a century ago, Hofmeister identified a sequence in the ability of salts to precipitate egg white (Vlachy et al., 2009). Today, this sequence refers to hydration. What he pointed out at that time is very important today, i.e. ions cannot be considered as isolated species in water.

Hydration phenomena are of great interest in the fields of physics, chemistry and biology (Paulaitis et al., 1996; Burakowski and Gliński, 2007). In the vicinity of an ion, the electrostatic interactions control the formation and the structuring of the hydration layer. Around organic molecules, hydration structures are much more complex and are the subject of many investigations. Indeed, it is widely accepted that water molecules play a very important role in the structure, stability, function and recognition of organic molecules.

The hydration of organic molecules is due to the polarity of each hydroxyl group (OH), which gives and accepts a hydrogen bond. The hydrogen bond is one of the most important non covalent interactions encountered in the natural sciences. These bonds, rather weak in energy, have a decisive influence on the chemical properties of substances. Since Pauling's publication, which focused on the nature of chemical bonds (Pauling, 1939), the hydrogen bond is commonly mentioned to explain properties of water, saccharides, or nucleic acids. These bonds play a key role in the solvation of molecules and more generally in solute/solvent interactions.

Many experimental and theoretical methods have been developed to describe the hydration phenomenon of saccharides, and more particularly their hydration number. Despite the interest in describing saccharide hydration, it is still difficult to quantify the number of water molecules that hydrate saccharides. Indeed, the definition of the hydration number depends on the experimental method adopted, the analytical model used, and the more or less confused understanding of the global hydration mechanism. The problem is therefore largely due to the different definitions of species hydration and to the method of determination used (Shiraga, Ogawa, Kondo, Irisawa, & Imamura, 2013), which leads to a large disparity in the saccharides hydration numbers values (Zavitsas, 2001; Galema and Høiland, 1991; Mathlouthi and Hutteau, 1999). Some authors have been interested in the link between the stereochemistry of the molecules and their hydration number, and more specifically a relationship between the saccharide hydration and the OH groups position (equatorial or axial position). For instance, Galema et al. (Galema & Høiland, 1991) reported that hexoses with an OH group in equatorial position (2) and an OH group in axial position (4), such as D galactose (1e2e3e4a6e), were the least

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compatible with the water structure. They disturb the water structure more than hexoses with an OH group in equatorial or axial position (2) and an OH group in equatorial position (4), such as D Glucose (1e2e3e4e6e). Consequently, hexoses with an equatorial OH group (2) and an axial OH group (4) have higher hydration numbers than other hexoses. Banipal, Hundal, and Banipal (2010) further confirmed that D arabinose (1e2e3e4a) with an OH group in equatorial position (2) and an OH group in axial position (4) has a greater disruptive effect on the three dimensional water structure than D xylose (1e2e3e4e), its con formation not being compatible with the water structure. Other studies have also confirmed the idea that saccharide compatibility with water depends on the number of hydroxyl groups and oxygen atoms, but also on the relative position of hydroxyl groups (Banipal et al., 2010; Seuvre and Mathlouthi, 2010; Banipal et al., 2015).

Some studies of molecular dynamics have focused on the effects of solvent on saccharide structure. For example, Winger et al. have shown the importance of hydrogen bonds for the stability of amylose and cellulose (Winger, 2008). The study of the behaviour of α D glucopyr anose, i.e. glucose, in aqueous solution, showed that water does not influence the configuration of the pyranose cycle (Brady, 1989). An other study highlighted the dependence of the β Cyclodextrin config uration (oligosaccharide) on the type of solvent (Boonyarattanakalin, Wolschann, & Lawtrakul, 2011). Finally, Ramadugu et al. have shown that the structure and dynamics of water on the surface of carbohy drates are determined by the type of binding between monomers and the anomeric configuration of saccharides (Ramadugu, Chung, Xia, & Margulis, 2009).

Few studies of molecular dynamics have focused on the hydration properties of saccharides. One concerns glucose and water interactions, published by Suzuki et al. (Suzuki, 2008). They used molecular dy namics to show that each hydroxyl group in glucose forms two hy drogen bonds with water molecules.

Saccharides can affect the structure of the surrounding water and, conversely, water can affect the structure of saccharide molecules. To better understand the saccharides functionality, interactions at the molecular level still need to be further explored. A recent review on the molecular applications of molecular dynamics in the food industry in dicates the need to focus research efforts on the hydration and solvation of saccharides (Feng et al., 2015). The difficulty in using molecular dynamics lies in choosing a model that correctly describes the water structure around molecules (Te, Tan, & Ichiye, 2010).

The thermochemical, structural and vibrational properties of a system containing hydrogen bonds can be described by quantum me chanics. Indeed, the theory of the functional density (DFT), applied to systems containing hydrogen bonds, is very efficient and allows inter action energies to be determined with great precision. Thus, theoretical studies, using quantum mechanics, have been undertaken on the hy dration properties of small species to describe hydrogen bonds (Bankura and Chandra, 2012; Bankura et al., 2013). For example, the hydration structure of OH $(H_2O)_n$ groups (n = 4, 8, 16 and 20) was investigated using quantum mechanics calculations (Bankura & Chandra, 2012). These quantum mechanics calculations have shown that the solvation structure of the hydroxide ion depends on the water molecules number. Recently, work using the density functional theory approach (DFT) has focused on the glucose hydration properties in water (Fuoco, Galier, Roux de Balmann, & De Luca, 2015) and shown that eleven water molecules stabilize glucose.

There has been renewed interest in characterizing and under standing the interactions between saccharide and electrolytes over the past 20 years (Seuvre and Mathlouthi, 2010; Banipal et al., 2015; Zhuo et al., 2000; Warmińska, 2012). The development of thermodynamic methods for determining the properties of saccharides in aqueous electrolytic solutions is gaining interest. Different thermodynamic methods are used to characterize saccharide/electrolyte interactions and species hydration properties (Shiraga et al., 2013; Banipal et al., 2015; Singh et al., 2015; Pal and Chauhan, 2009). Thermodynamic quantities, such as the partial molar volume heat capacity (Banipal, Banipal, Ahluwalia, & Lark, 2002) or the apparent molar volume (Banipal et al., 2015; Shekaari and Kazempour, 2012), provide in formation on solute/electrolyte interactions and the solutes hydration properties. For example, the variation in the apparent molar volumes of sucrose in the presence of NaCl and KCl has been attributed to the dehydration of the saccharide in presence of electrolyte (Sangster, Teng, & Lenzi, 1976). These results were later confirmed by other studies (Zhuo et al., 2000; Banipal et al., 2002). Recently, in the field of membrane separation, volumetric properties, which characterizes the saccharide hydration, have been used to understand the increase of the mass transfer of xylose, glucose, and saccharose through nanofiltration membranes in the presence of electrolytes (Boy, Roux de Balmann, & Galier, 2012).

Although researches on saccharides have focused on the develop ment of experimental methods to study the hydration phenomena in the presence of electrolyte, the understanding of interaction mechanisms at the molecular level still needs to be further developed. Thus, it is ne cessary to develop new complementary approaches to accurately assess the contribution of interactions in solution. In this context, molecular simulation, and more particularly quantum mechanics, can provide information that is not directly accessible by experimental techniques.

Thus, quantum mechanics is particularly adapted to the study of interactions between saccharides and ions. However, to our best knowledge, these interactions have never been studied in the presence of water molecules. Moreover, no systematic study with different sac charides/monovalent or divalent cations/water systems has been car ried out. The lack of data makes it difficult to understand the re lationship between interactions in these systems, ion characteristics (charge, size and hydration) and solutes hydration properties.

In our previous work, the saccharides hydration numbers (xylose, glucose, sucrose) have been calculated in various electrolytes (LiCl, NaCl, KCl, Na_2SO_4, K_2SO_4, $CaCl_2$, $MgCl_2$, $MgSO_4$), for different ionic compositions, from thermodynamic data (Teychené, Roux De Balmann, & Galier, 2017). It has been shown that the saccharide hydration number decreases with the increase of the electrolyte molality, de pending on the electrolyte nature. On the other hand, ions hydration properties were also computed using theoretical methods (DFT) (Teychené, Balmann, Maron, & Galier, 2018).

Saccharide and ions properties obtained from thermodynamic data and simulation works respectively, were then put in parallel, in order to rationalize the relation between the saccharide hydration number in electrolytic solution and the hydration properties of ions (Teychené et al., 2018). The study shown that the saccharide dehydration in creases with increasing cation coordination number (i.e. the number of water molecules in direct interaction with the cation), regardless of the valence of the cation. Divalent cations have a greater impact on sac charide dehydration than monovalent cations. For a given cation va lence, the cation coordination number increases with the size of the cation. This allows the cation to create more interactions with the saccharide hydroxyl groups and then to further dehydrate the sac charide. Thus, this work highlighted that the cation coordination number reflects the ions ability to form direct interactions with the saccharide hydroxyl groups and thus their ability to dehydrate sac charide.

In our previous work (Teychené, Roux de Balmann, Maron, & Galier, 2019), a methodology using a quantum mechanics method (DFT) has been implemented in order to describe the hydration prop erties of ions in water in different systems (LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$ and $MgSO_4$). Results shown that the presence of anions (Cl or SO_4^{2-}) does not lead to structural and energetic changes in the cation first hydration layer (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}). Considering that anions (Cl or SO_4^{2-}) do not influence the hydration characteristics of the cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}), the objective of this work is therefore to study interactions in saccharide/cation/water systems using quantum mechanics to understand the link between saccharides

hydration and the cation. The study of many systems will make it possible to generalize the obtained results: xylose, glucose and sucrose will be mixed to various cations (Li^+, Na^+, K^+; Mg^{2+}, Ca^{2+}) and a variable number of water molecules.

The approach envisaged is based on the study of systems of increasing complexity. First, the saccharides hydration properties are characterized in presence of water molecules. In a second step, the interactions are evaluated in saccharide/cation/water systems and compared to the results obtained in saccharide/water systems and in ion/water systems.

2. Methodology

2.1. Saccharide/water system

The solute hydration properties were carried out at the DFT level of theory, the B3PW91 functional (Becke, 1993) and 6 31 + +G** basis sets with the Gaussian 09 suite of programs (see Supporting Information for details). Geometries were fully optimized in gas phase at 298.15 K and 1 atm, without symmetry constraints, employing the hybrid density functional B3PW91 (Becke, 1993). Potential surfaces energy, as well as optimized geometries, do not depend on temperature and pressure. However, thermochemistry, as enthalpy and entropy, are temperature dependent.

For the Li, Na, K, Mg, Ca, H, O, and C atoms, a double zeta 6 31G (Frisch & Pople, 1984) basis set augmented by a polarization function was used.

Quantum mechanics calculations were performed for 3 saccharides: xylose, glucose and sucrose. The saccharides initial structures forms used for the optimization calculations, are those predominant in water: isomeric forms β for xylose and glucose (Poonia & Bajaj, 1979). Sucrose is a disaccharide formed by a glucose molecule and a fructose molecule, linked by an osidic bond.

The hydroxyl (OH) and ether oxide (O) groups of saccharides interact preferentially with water molecules. Each hydroxyl group can participate in up to 3 hydrogen bonds and intracyclic oxygen can participate in 2 hydrogen bonds (Molteni & Parrinello, 1998). The enthalpy optimization calculations are thus carried out by adding one water molecule at time in a stepwise manner, in order to construct the saccharide hydration shell. The optimization is performed at each step, without any symmetry constraints. The saccharide hydration enthalpy, $H_{S/W}$, is calculated as the difference between the enthalpy of the complex ($H_{complex}$) and those of the two separated fragments, namely the saccharide (H_S) and the water cluster (H_W):

$$H_{S/W} = H_{complex} - H_S - H_W \quad (1)$$

The saccharide first hydration shell is considered to be complete when the interaction enthalpy between the saccharide and the water ($H_{S/W}$) reaches a plateau, i.e., is stable with respect to water addition, as defined by Eq. (1). On these structures, the saccharide coordination number is defined as the number of water molecules in direct interaction with the oxygen or hydrogen atom of the saccharide hydroxyl groups. A water molecule is considered in direct interaction if hydrogens bonds are established between the hydrogen and the oxygen, that means a donor acceptor distance between 1 Å (covalent O—H distance) and 2.5 Å (Koch & Holthausen, 2001).

The saccharides hydration properties are thus characterized by their coordination number, CN, the distance between the saccharide and the coordinated water molecules, $d_{S/W}$, and the saccharide hydration enthalpy $H_{S/W}$.

2.2. Saccharide/cation/water system

Quantum mechanics calculations were used to study interactions in system containing the saccharide, the cation and water molecules.

Monovalent and divalent cations (Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) were added near the central oxygen atom of the saccharides (ether oxide for glucose and xylose, oxygen of the osidic bond for sucrose). A preliminary calculation of the structure [saccharide + cation] was performed. Then, the calculations are carried out by adding one by one the water molecules to the last optimized structure.

The saccharides and ions hydration properties are thus characterized by their coordination number, CN, the distance between the specie and the coordinated water molecules, and the species hydration enthalpy.

3. Results

3.1. Saccharide/water systems

The molecular coordinates of the atoms of saccharide optimized structure are given in SI, as a function of the number of water molecules in the system.

When the conditions described in I.1 are verified, the saccharide first hydration shell is considered to be complete. For instance, Fig. 1 SI in Supporting Information shows that when the first 7 water molecules are added to the system, the xylose variation hydration enthalpy is very high. The saccharide hydration is not stable and the first water layer coordinated to the saccharide is not complete. The derivative of xylose hydration enthalpy relative to the number of water molecules changes sign when the 8th water molecule is added to the system (Table 1 SI). From the 9th water molecule, an energy plateau is reached and the added water molecules structure the water network. The value of the hydration enthalpy derivative decreases in accordance with the appearance of the first full hydration layer. Finally, on the plateau, the xylose coordination number is stable, between 7 and 8 water molecules (Table 1 SI). More precisely, 8 water molecules mainly coordinate xylose, at a distance between 1.92 and 1.94 Å from the xylose. The hydration enthalpy of xylose, corresponding to the value of the average enthalpy obtained at the plateau, is -270 kJ.mol^{-1}. A second energy plateau is reached around -350 kJ.mol^{-1}. This plateau corresponds to the formation of the second hydration layer of xylose. As the second layer is structured, the xylose coordination number increases. Indeed, it varies from 8 water molecules, at a distance between 1.92 Å and 1.94 Å from the saccharide, to 10 molecules of water, at a distance of about 1.78 Å. The appearance of the second hydration layer has an impact on the structuring of the first hydration layer. Indeed, it causes the water molecules around the saccharide to move closer and thus increases the number of water molecules coordinated to the saccharide. The second hydration layer has much less impact on the stability of the xylose than the water molecules coordinated to the saccharide. Indeed, the additional hydration enthalpy provided by the second layer of solvation is about -80 kJ.mol^{-1}, while the first one represents -270 kJ.mol^{-1}. These values show that the enthalpy stability of xylose is mainly ensured by its first hydration layer.

The characteristic values of the saccharide hydration properties are summarized in Table 1, that means the saccharide coordination number, CN, the average distance between the saccharide and the water molecules, $d_{S/W}$, the saccharide solvation enthalpy, $H_{S/W}$ and the hydration enthalpy calculated per hydrophilic group in each saccharide, $H_{S/W/O}$. For comparison, results from other studies are also reported.

Saccharide coordination numbers, CN, are dependent on the method used. The problem is largely due to the different definitions of a specie hydration and the method of determination used. In thermodynamic measurements, only the water molecules directly interacting with the saccharide hydrophilic groups are taken into account, whereas viscosity and acoustic measurements consider all the water around the solute surface. Molecular simulation takes into account the overall number of water molecules disturbed by the presence of the solute. Only one study, based on compressibility measurements, reports the coordination number of the 3 saccharides (Galema & Høiland, 1991). These values were also reported by Mathlouthi et al. for the glucose and the sucrose,

Table 1
Saccharide hydration properties in pure water at 298.15 K with: – CN: saccharide coordination number – $d_{S/W}$: distance between the saccharide and the coordinated water molecules – $H_{S/W}$: saccharide hydration enthalpy – O number: saccharide hydrophilic group number – $H_{S/W/O}$: hydration enthalpy of each hydrophilic group in saccharide.

	Xylose	Glucose	Sucrose
CN	7–8 (rather 8) 6.8 (Galema & Høiland, 1991)	8–10 (rather 9) 3.01 (Mathlouthi & Hutteau, 1999) 8.4 (Galema & Høiland, 1991)	14–16 (rather 16) 6.14 (Mathlouthi & Hutteau, 1999) 13.9 (Galema & Høiland, 1991) 13.8;14.1 (Branca et al., 2001)
$d_{S/W}$ (Å)	1.92–1.94	1.74–1.79	1.86–1.87
$H_{S/W}$ (kJ.mol ^{1})	270	370 to 424 (Fuoco et al., 2015)	600
O number	5	6	11
$H_{S/W/O}$ (kJ.mol ^{1}/hydrophilic group)	54	62	55

from viscosity measurements (Mathlouthi & Hutteau, 1999). Sucrose values were obtained from acoustic and ultrasonic measurements (Branca et al., 2001). Although the methods used are different, the coordination number values follow the same trend to those obtained in our study, indicating the validity of our approach and assumptions. Regardless of the method, disaccharide hydration numbers are higher than those of monosaccharides. Results confirm that the hydration number varies with the number of OH and O groups in saccharide (4 OH and 1 O for xylose, 5 OH and 1 O for glucose, 8 OH and 3 O for sucrose).

The glucose hydration enthalpy obtained in another study using the same approach is also reported (Fuoco et al., 2015). The difference between the two values (370 kJ.mol^{-1} in the present work, compared to -424 kJ.mol^{-1}) can be explained by the temperature conditions. Indeed, the glucose hydration enthalpy was calculated from the internal energy of the system at 0 K in the other work, while in our study, it is calculated from the enthalpy at 298.15 K.

The saccharides coordination numbers, CN, and their hydration enthalpy, $H_{S/W}$, increase with the saccharide size, according to the following sequence (Table 1):

Xylose < Glucose < Sucrose

This sequence confirms that the hydration number depends on saccharide hydrophilic group number. The coordination number and the hydration energies are consistent with the number of hydrogen bonds that saccharides are able to form with water.

Finally, the $H_{S/W/O}$ values (hydration enthalpy per saccharide hydrophilic group), reported in Table 1, show that each saccharide hydrophilic group (O and OH) interacts with water molecules, with an enthalpy between -54 and -62 kJ.mol^{-1}. The hydration energies relative to the hydrophilic groups number are thus very similar whatever the saccharide.

Concerning the saccharide structure, the saccharide O—H bonds lengths are about 0.96 Å without water in the system. Adding water in the system has the effect of lengthening this bond by 0.03 Å on average. The saccharide C—O bonds lengths are not affected by the water molecules.

3.2. Saccharide/cation/water systems

3.2.1. Saccharide/water interactions

Results from quantum mechanics calculations in system containing the saccharide, the cation and water molecules are reported in Table 2 SI. The saccharide coordination number, CN, and the distance between the saccharide and the coordinated water molecules, $d_{S/W}$, obtained when saccharides are in pure water or in the presence of cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}), are also indicated.

The impact of cations on saccharide hydration is discussed by comparing the saccharide hydration properties in pure water and in presence of cations.

The saccharides coordination numbers, CN, in the presence of cations, decrease compared to those in pure water (Table 2 SI), with the exception of the glucose/Li^+/water system. No trends can be clearly identified.

From the analysis of the distance between saccharide and coordinated water molecules, $d_{S/W}$, results show that in the presence of cation, $d_{S/W}$ decrease with the exception of glucose/K^+/water and glucose/Na^+/water systems for which a slight increase in distance is observed.

Monovalent and divalent cations (Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) were added near the central oxygen atom of the saccharides (ether oxide for glucose and xylose, oxygen of the osidic bond for sucrose). Saccharide oxygens atoms near the cations orient to the cations and interact with them. For sucrose, the presence of cations has the effect of structuring the saccharide around the cation. Its shape changes and becomes more or less tight around the cation, depending on the cation present (see next section).

By focusing on the interactions between the ions and the saccharide oxygen interacting with this ion, a trend can be established. For example, Table 3 SI details distances between glucose oxygen atoms and interacting ions.

In presence of monovalent ions, the distance glucose oxygen atoms and ions in interaction increases in the following order:

$Li^+ < Na^+ < K^+$

In presence of divalent ions, this distance increases in the following order:

$Mg^{2+} < Ca^{2+}$

Li^+ and Mg^{2+} have higher charge densities than other ions of the same valence, their interaction with saccharide is more important. The consequence is that Li^+ and Mg^{2+} are closer to the saccharide oxygen with which it interacts, than other ions of the same valence.

Results indicate that the distance between the oxygen in the saccharide and the interacting ions is a compromise between the ion charge but also its size. By comparing ions of different valence, for instance, Mg^{2+} and Li^+, Mg^{2+} has higher charge density than Li^+ but is larger than Li^+. That means Mg^{2+} should get closer from saccharide than Li^+ but its steric hindrance prevents it from getting closer to the saccharide. Interestingly enough, these results match the one found in pure water (Teychené et al., 2019). Same trends are observed for xylose and sucrose.

Concerning the saccharide structure, the saccharide O—H bonds lengths remains 0.99 Å in presence of cations in pure water (same value as saccharide in pure water without cation) meaning cations do not affect the length of the O—H bonds. Likewise, the saccharide C—O bonds lengths are not affected by the cations presence.

Results concerning the saccharide hydration enthalpy, $H_{S/W}$, are reported in Table 4 SI and drawn in Fig. 1.

The presence of cations reduces the hydration enthalpy of

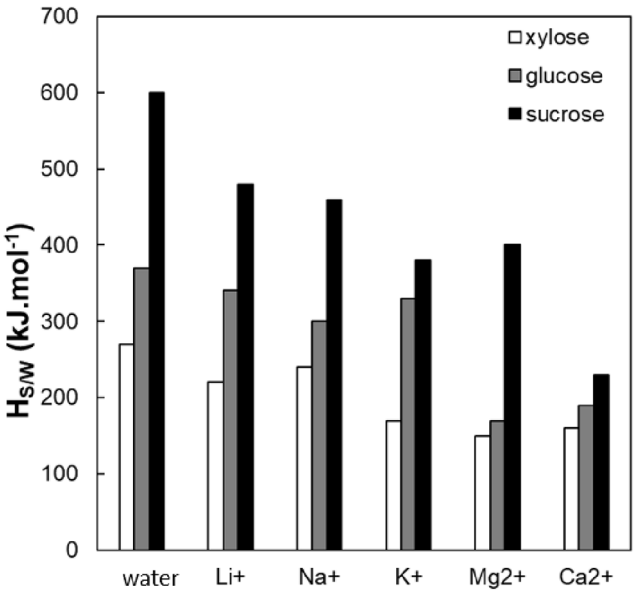

Fig. 1. Saccharide enthalpy hydration, $H_{S/W}$ (in absolute value), in pure water and in the presence of cations/water molecules, at 298.15 K.

saccharides, $H_{S/W}$ (Table 4 SI and Fig. 1). This variations clearly show the dehydration of saccharide, depending on the cation. In accordance with the results obtained in pure water, whatever the cation, the sac charide hydration enthalpy in presence of cations remains identical to that observed in water (Xylose < Glucose < Sucrose). As mentioned above, this sequence is directly related to the saccharide hydrophilic group numbers.

Concerning the influence of the nature of ions, Fig. 1 shows that the decrease in saccharide hydration enthalpy is greater in the presence of divalent cations, compared to monovalent cations, with the exception of sucrose/K^+/H_2O and sucrose/Mg^{2+}/H_2O systems, for which similar hydration energies are obtained. Thus, saccharide dehydration is more important in the presence of divalent cations than in the presence of monovalent cations.

The variation in sucrose hydration enthalpy in the presence of monovalent cations clearly shows that sucrose dehydration increases in the following order:

$$Li^+ < Na^+ < K^+$$

Smaller variations in hydration enthalpy for xylose and glucose are observed, because of their smaller number of hydroxyl groups com pared to sucrose. In consequence, no trends concerning the impact of cation on their hydration enthalpy can be drawn.

With regard to the impact of divalent cations, results show that sucrose dehydration increases according to the following sequence:

$$Mg^{2+} < Ca^{2+}$$

As mentioned above, variations in hydration enthalpy are more significant for sucrose due to its greater hydroxyl group numbers.

3.2.2. Cation/water interactions

The coordinated cation number, CN, as well as the distance between the cations and the coordinated water molecules, $d_{C+/W}$, in pure water and in presence of saccharides, are reported in Table 2.

A clear decrease in the cation coordination number in the presence of saccharide (Table 2) can be noticed. In addition, the presence of sucrose causes a greater CN decrease compared to that obtained in the presence of xylose or glucose and the decrease in the cation coordina tion number is more significant for divalent cations than for mono valent ones. The impact of xylose and glucose on the cation coordina tion number cannot be differentiated.

Concerning the distances between the cation and the coordinated water molecules, $d_{C+/W}$, due to the small variations observed, no trends according to the nature of the saccharides can be observed. However, for all saccharides, $d_{C+/W}$ follows the same trends as the one observed in pure water ($Li^+ < Na^+ < K^+$ and $Mg^{2+} < Ca^{2+}$).

The results concerning the cation hydration enthalpy, $H_{C+/W}$, in pure water, and in the presence of saccharides, are reported in Table 5 SI.

Results indicate that the presence of saccharide causes a decrease in cation hydration enthalpy, $H_{C+/W}$ (Table 5 SI). This decrease is asso ciated with the dehydration of cations, induced by the presence of saccharide.

The variation of cation hydration enthalpy in pure water and in the presence of saccharides is shown in Fig. 2. One can observe that the cations dehydration depends on the saccharide. Sucrose dehydrates cations more than xylose or glucose does. As mentioned above, this result is in agreement with the greater hydrophilic group number of sucrose, as compared to the other two saccharides. Indeed, cations can form more interactions with sucrose than xylose and glucose. Moreover, this result is consistent with the greater decrease of the cations co ordination number in the presence of sucrose.

In addition, Fig. 2 shows that the presence of saccharides does not change the variation sequence of the cation hydration enthalpy. Indeed, in pure water, as in the presence of saccharides, the following sequence is preserved:

$$K^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+}$$

Finally, the cations dehydration in presence of saccharides is high lighted and quantified by the decrease of their coordination number as well as their hydration enthalpy.

3.2.3. Saccharide/cation interactions

The study of interactions between saccharides and cations is based on the determination of the number of interactions between the cation and the oxygen of saccharides as well as on the interaction enthalpy values between saccharide and cation. The number of interaction be tween the cation and the oxygen is the number of oxygen atom (from saccharide) directly in interaction with the ion. An oxygen atom is considered in direct interaction with the ion, if the length of the bond is shorter than the sum of the van der Waals radii of the interacting atoms (Teychené et al., 2019).

The interaction numbers values, $n_{inter\ S/C+}$, between the cation and saccharide are given in Table 6 SI. Cation coordination numbers in pure water and in the presence of saccharides are also reported for discus sion.

The saccharide/cation interaction numbers are greater in the pre sence of sucrose than in the presence of xylose or glucose, with the exception of the interaction numbers in presence of Li^+ which are identical for all three saccharides. For Li^+, this phenomenon can be associated with the steric hindrance around this ion, which limits the number of interactions with saccharides.

Therefore, a relationship is established between the saccharide de hydration and cations, and the number of hydrophilic groups in sac charide. Indeed, the number of interactions between the saccharide and the cation increases with the hydrophilic group numbers of saccharide. Consequently, saccharides and cations are more dehydrated. In addi tion, xylose and glucose, which have similar hydrophilic groups num bers, have, for a given cation, close $n_{inter\ S/C+}$ values.

The evolution of the interactions number, $n_{inter\ S/C+}$, for the dif ferent saccharides, in the presence of the cations, is shown in Fig. 3. It appears that the interaction numbers between divalent cations and saccharides is greater than that between monovalent cations and sac charides. This is consistent with previous observations. Moreover, for the three saccharides, the saccharide/cation interactions number in creases as the cations coordination number in pure water (Table 6 SI):

Table 2
Hydration properties of Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} in pure water and in the presence of saccharides/water molecules, at 298.15 K: – CN: cation coordination number – $d_{C+/W}$: average distance between cations and the coordinated water molecules.

		Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
CN	Pure water	4	5	6	6	8
	Xylose	2	3	3	2	4
	Glucose	3	3	3	3	5
	Sucrose	2	3	2–3	1	2
$d_{C+/W}$ (Å)	Pure water	1.99–2.11	2.38–2.49	2.81–2.92	1.95–2.13	2.44–2.52
	Xylose	1.96–2.07	2.27–2.30	2.77–2.87	2.03–2.05	2.41–2.44
	Glucose	2.00–2.02	2.43–2.50	2.75–2.86	2.05–2.13	2.34–2.54
	Sucrose	1.95–1.99	2.40–2.42	2.74–2.78	2.04–2.05	2.38–2.62

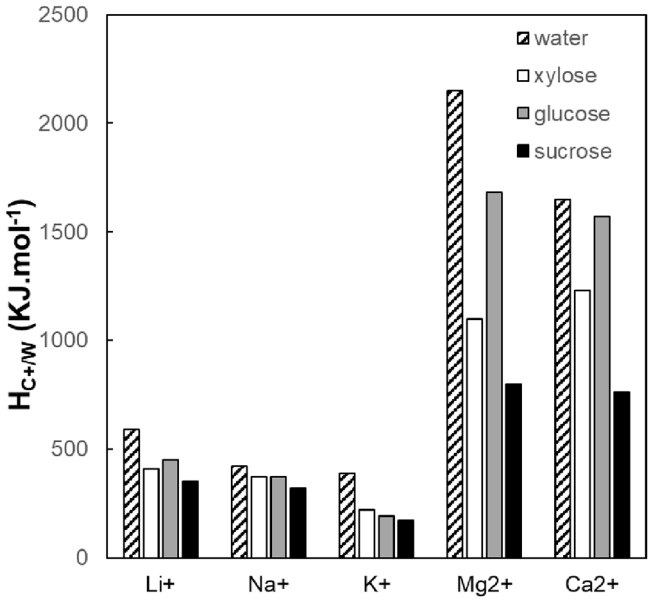

Fig. 2. Cation enthalpy hydration, $H_{C+/W}$ of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in pure water and in presence of saccharides (in absolute value)/water molecules, at 298.15 K.

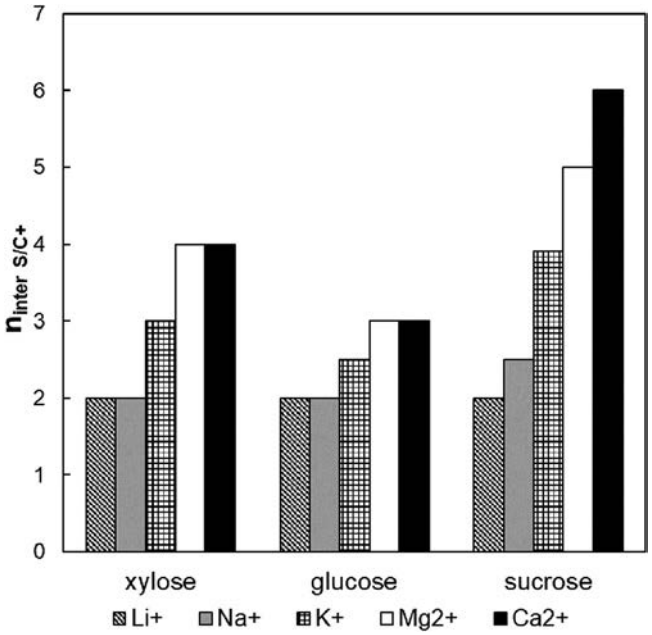

Fig. 3. Variation of the saccharide/cation interaction numbers $n_{inter\ S/C+}$, at 298.15 K: influence of the nature of the cations.

$$Li^+ \leq Na^+ < K^+ \leq Mg^{2+} < Ca^{2+}$$

In our previous work, a systematic volumetric study of saccharides (xylose, glucose and sucrose) in the presence of various electrolytes (LiCl, NaCl, NaCl, NaCl, KCl, Na_2SO_4, K_2SO_4, $CaCl_2$, $MgCl_2$ and $MgSO_4$) was carried out using density measurements at 298.15 K (Teychené et al., 2017). From these data, the saccharide hydration number at in finite dilution, which explicitly reveals the degree of hydration of the solute, has been calculated for different ionic compositions (Teychené et al., 2018). With regard to the impact of the cation, results shown that the saccharide dehydration increases according to the following se quence:

$$Li^+ < Na^+ < K^+ \leq Mg^{2+} < Ca^{2+}.$$

This sequence, identified from the saccharide hydration number, is consistent with results of the present simulation work.

In summary, results show that saccharides are all the more dehy drated as the saccharide/cation interaction number increases, which in turn increases with the cations coordination numbers, CN, in pure water.

In addition, the cation coordination number decrease is approxi mately equal to the number of saccharide/cation interactions (Table 6 SI). In other words, the sum of the cation coordination number in the presence of saccharide, and of the saccharide/cation interaction number, is constant, and equal to the cation coordination number in water:

$$\mathbf{CN_{cation+water}} = \mathbf{CN_{cation+saccharide}} + \mathbf{n_{inter\ S/C+}} \quad (2)$$

For example, in pure water, the Mg^{2+} ion has six direct interactions with water molecules. In the presence of sucrose, five Mg^{2+}/water molecules interactions are replaced by Mg^{2+}/saccharide interactions while the Mg^{2+} ion keeps only one direct interaction with the water molecules (Fig. 2 SI).

In the presence of saccharide, a fraction of the cation/water OH group interactions is replaced by cation/saccharide hydrophilic group interactions.

Thus, cations interact with the same number of hydrophilic groups, in water or in the presence of saccharide. This observation raises questions about the geometric structure of oxygen atoms around cations in the presence of saccharide. Is the structure of the oxygen atoms network around the cations affected by the presence of saccharide?

In order to answer this question, the geometry of the oxygen net work structure is analyzed within the different saccharide/cation/water systems and compared to the cations geometry in cation/water systems. Results of this study are detailed in Table 7 SI. They show that the structure of the oxygen atoms coordinated with the cations is the same in the presence of saccharide as in pure water. This remark is consistent with the ability of cations to retain the same number of oxygen atoms, whether or not there is a saccharide in solution. However, a deforma tion of the network of oxygen atoms coordinated with the cations can be observed in the presence of saccharide. For instance, in pure water, the arrangement of oxygen molecule belonging to water around Mg^{2+}

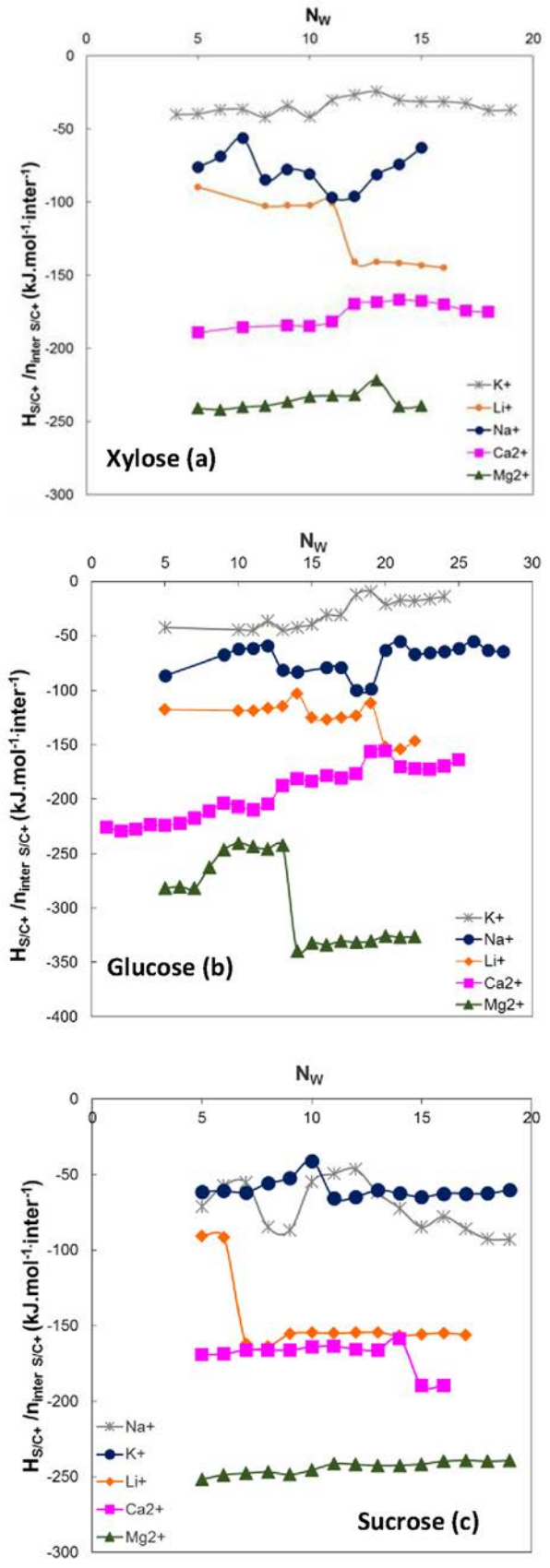

Fig. 4. Variation of saccharide/cation interaction enthalpy, related to the number of saccharide/cation interactions, $H_{S/C+}/n_{inter\ S/C+}$, as function of the water molecules number N_W, at 298.15 K: Influence of the nature of the cation. Xylose (a), Glucose (b), Sucrose (c).

is a regular octahedral. In presence of saccharide, the arrangement of oxygen molecule belonging to saccharide around Mg^{2+} still remains a octahedral but is irregular.

The saccharide/cation interaction energies are distributed over each of the saccharide/cation interactions. Thus, the values of these energies are divided by the saccharide/cation interaction numbers, $n_{inter\ S/C+}$, in order to compare them. The evolution of the saccharide/cation inter action energies, related to the interaction numbers, is represented in Fig. 4, as a function of the water molecules numbers in the system, N_w.

The abrupt energetic variations observed in Fig. 4 correspond to changes in the number of saccharide/cation interactions that can sud denly vary by one unit.

The results show that, for the three saccharides, the saccharide/ cation interaction energies, related to the saccharide/cation interaction numbers, increase in the following order:

$$K^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+}$$

This sequence is identical to that obtained for the variation of the cation hydration enthalpy in pure water or in the presence of saccharide (Teychené et al., 2018). Thus, the saccharide/cation interaction en ergies increase with the cations hydration enthalpy.

Table 8 SI summarizes the values of the average interaction en ergies, related to the saccharide/cation interaction numbers.

For a given cation and whatever the saccharide, the results reported in Table 8 SI show that the saccharide/cation interaction energies, re lative to the interaction numbers, are close. Thus, for a given cation, the saccharide/cation interaction enthalpy, related to the interaction number, is independent of the nature of the saccharide.

In summary, the hydration properties study has shown that sac charides and cations are both dehydrated in saccharide/cation/water system. In addition, their interaction essentially impacts the water molecules coordinated with saccharide and cation.

With regard to the influence of the nature of the saccharide, the higher the number of hydrophilic groups in the saccharide, the more important is the dehydration of the cations. In addition, the presence of saccharide does not change the order of variation of cation hydration energies obtained in water:

$$K^+ < Na^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+}.$$

The variation of the saccharide hydration enthalpy is greater in the presence of divalent cations than in the presence of monovalent ones and the saccharide dehydration in the presence of cations increases according to the following sequences: $Li^+ < Na^+ < K^+$ and $Mg^{2+} < Ca^{2+}$.

Finally, saccharides are all the more dehydrated as the saccharide/ cation interaction number increases, which in turn increases with the cation coordination number in pure water.

4. Conclusion

The objective of the work was to explain the saccharide dehydration observed in presence of electrolyte at the experimental scale, by the characterization and the understanding of interactions between sac charides and cations and water molecules using a quantum mechanics approach. Based on the results obtained in this work, a relationship was established between the saccharides properties, the ion characteristics (charge, size and hydration) and the solutes hydration properties.

In the first part of this work, the hydration properties of xylose, glucose and sucrose in pure water were determined at the molecular level using a quantum mechanics method. Results show that the sac charide coordination numbers, defined as the number of water mole cules directly linked to saccharide, as well as the saccharides hydration enthalpy, increase with the saccharide hydrophilic group numbers.

In the second part, the study focused on the interactions in sac charide/cation/water systems. The influence of the presence of the

cation on saccharide hydration properties and of the presence of saccharide on cation hydration properties was evaluated by comparison with the results obtained in the saccharide/water and ion/water systems.

In saccharide/cation/water systems, the decrease in cation and saccharide energies enthalpy highlighted that that both solutes are dehydrated compared to solute/water systems.

With regard to the cation coordination number, this study shows that cations dehydration increases with the saccharide hydrophilic group number. Moreover, the presence of saccharide does not modify the cation hydration enthalpy sequence observed in pure water:

$$K^+ < Na^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+}$$

Concerning the saccharide hydration, it has also been shown that saccharide dehydration is more important in the presence of divalent cations than in the presence of monovalent ones. The variation of the sucrose hydration enthalpy according to the nature of the cations shows that sucrose dehydration increases according to the following sequences: $Li^+ < Na^+ < K^+$ in the presence of monovalent cations and $Mg^{2+} < Ca^{2+}$ in the presence of divalent cations.

In addition, the sucrose dehydration sequence in presence of cations and water molecules is consistent with saccharide hydration number calculated from thermodynamic data in previous experimental work (Teychené et al., 2017; Teychené et al., 2018).

The dehydration sequence of saccharides was explained from the study of saccharide/cation interactions. It has been shown that saccharides are all the more dehydrated as the number of saccharide/cation interactions increases, which in turn increases with the cation coordination number in water. It is important to note that the sum of the cation coordination number in the presence of saccharide and of the saccharide/cation interaction numbers is constant, and equal to the coordination number of cation in water.

Finally, the relationship between the saccharides hydration numbers (calculated from experimental data [32]) and the cation coordination numbers has been rationalized through this work.

In this sense, an extension of this study by including trehalose, and even protein would be appropriate. Results in systems containing amino acids, ions, saccharide and water could rationalize the experimental results found by infrared spectroscopy in other work (Giuffrida, Cottone, & Cordone, 2017) in binary, ternary and even quaternary protein containing system.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2020.127054.

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